

# Preparation of Methyl Lactate

## CONTINUOUS ALCOHOLYSIS OF LACTIC ACID POLYMERS

E. M. FILACHIONE, J. H. LENGEL,  
AND C. H. FISHER

*Eastern Regional Research Laboratory  
U. S. Department of Agriculture, Philadelphia, Pa.*

**T**HE conversion of lactic acid into its esters is worthy of study because lactic acid can be made easily by fermentation (20, 21) from several carbohydrates, its esters are useful as solvents, plasticizers, or intermediates (27, 28), and its two functional groups can be used to prepare numerous derivatives. Preparation of methyl lactate in high yield by conventional methods is unusually difficult because methyl lactate distills azeotropically with water but methanol does not, and methyl lactate is readily hydrolyzed (25). Although esterification of lactic acid with methanol is troublesome, this operation is important because methyl lactate can be converted readily into higher lactic esters by alcoholysis (5) or into methyl acrylate by pyrolysis of its acetyl derivative (5, 29).

Methyl or ethyl lactate has been made by: (a) direct esterification (1, 2, 3, 7, 8, 11, 24, 34); (b) reaction of zinc ammonium lactate (12, 19, 22, 32, 35) with methanol in the presence of sufficient mineral acid to liberate lactic acid; (c) reaction of calcium magnesium, or sodium lactate (6, 15, 20, 26, 27, 33) with methanol in the presence of adequate quantities of mineral acid; (d) reaction of silver lactate (22, 23, 24, 31) with methyl iodide; (e) reaction of anhydrides or polymers (3, 4, 6, 9, 10, 13, 14) of lactic acid with methanol; (f) treating ethyl lactyl lactate with ethanol (16); and (g) heating calcium or sodium lactate with potassium thyl sulfate or with ethyl toluene sulfonate (17, 30).

The present paper describes the preparation (both batch and continuous) of methyl lactate by alcoholysis of lactic acid polymers, a method that for the most part avoids the difficulties encountered when water is present.

### PREPARATION OF LACTIC ACID POLYMERS

Polylactic acid used for the production of methyl lactate was prepared by batch or continuous methods (10). The batch method comprised distilling water from lactic acid under reduced pressures. The continuous method consisted in passing 82% lactic acid of edible grade (containing a small amount of sulfuric acid) down a heated column (Pyrex tube, 1 inch in diameter and 4 feet long) packed with small Berl porcelain saddles, withdrawing water vapor from the top, and removing the lactic acid polymers from the bottom of the column.

The extent of the dehydration and self-esterification of the lactic acid was usually estimated by the amount of water removed and by titration and saponification of the condensation polymers. At room temperature the polymers ranged from amber semi-solids to brown firm masses, depending upon the degree of dehydration. All the polymers were fluid at about 90° C.

### METHYL LACTATE FROM LACTIC ACID POLYMERS

**CLOSED-VESSEL EXPERIMENTS.** In experiments not described here it was found that methyl lactate can be produced in 50 to 65% yields by refluxing polylactic acid with methanol for about 10 hours in the presence of mineral acid catalyst. Higher yields, however, were obtained at somewhat higher temperatures in a closed vessel, and less reaction time was required (Table I). The results of several closed-vessel experiments indicated, however, that 100° C. for 1 hour is approximately as effective as 150° for the same period of time. High yields were obtained even when the mole ratio of methanol to available lactic acid was as low as 2.5.

The experimental procedure was as follows: The mixture of polylactic acid, methanol, and catalyst was placed in the reaction vessel ("magnesia" bottle for 100° C. and glass-lined bomb for

150° C. experiments) and heated for several hours. The catalyst was neutralized with sodium acetate; methanol and a small amount of water were distilled at atmospheric pressure; and methyl lactate was distilled under diminished pressure (Table I). No correction was made for the small amounts of methyl lactate that distilled azeotropically with water.

**CONTINUOUS METHOD.** In other experiments it was found that methyl lactate can be made continuously and in high yields by passing methanol vapor through polylactic acid, withdrawing methanol and methyl lactate vapors from the reaction vessel, and passing the mixed vapors into continuous distillation equipment.

In one series of experiments (Table II), the reaction vessel was a cylindrical chamber 8.5 inches high and 2.75 inches in diameter. A fritted-glass plate at the bottom, through which methanol vapor was passed, dispersed it as small bubbles over the entire cross section of the reaction vessel. Polylactic acid containing esterification and alcoholysis catalysts, such as sulfuric or toluenesulfonic acids, was introduced into the reaction vessel through a separatory funnel. The vessel was immersed in an oil bath maintained at reaction temperature. The vapors withdrawn from the top consisted mainly of methanol and methyl lactate. The condensed mixture was distilled at atmospheric pressure to remove methanol and under reduced pressure to recover the methyl lactate. Virtually all the material placed in the reaction vessel was volatilized; the principal by-product was distillation residues.

In another series of experiments, methyl lactate was prepared by treating lactic acid polymers with methanol vapor in a tower (1 inch in diameter and 4 feet long) packed with small Berl porcelain saddles. Condensation polymers, as such or dissolved

TABLE I. METHYL LACTATE FROM POLYLACTIC ACID (CLOSED-VESSEL EXPERIMENTS)

Expt. No.	Poly-lactic acid equivalent, mole	Equivalents, wt.*	Ratio, Methanol/Lactic Acid	Concd. H <sub>2</sub> SO <sub>4</sub> , Ml.	Temp., ° C.	Time, Hr.	Conversion to Methyl Lactate, %
130	0.5	..	2.5	0.25	150 ± 5	4	75-8
132-7	0.5	..	2.5	0.5	150 ± 5	4	78-83
157	0.5	79	1.0	0.5	150 ± 5	4	33
164	0.5	79	2.5	0.5	150 ± 5	2	73
165	0.5	79	2.5	0.5	150 ± 5	1	76
166	0.5	79	1.0	0.5	100	4	51
167	0.5	79	2.5	0.5	100	4	76
168	0.5	79	5.0	0.5	100	4	75
169	0.5	79	10.0	0.5	100	4	78
170	0.5	79	5.0	0.5	100	2	78
173	0.5	79	5.0	0.5	100	1	84
181	1.0	77	2.5	1.0	100	4	76
182	1.0	77	5.0	1.0	100	4	75
184	1.0	77	2.5	0.5	100	4	79
185	1.0	77	2.5	0.25	100	4	80
195	0.5	77	5.0	1.0	100	4	81
199	0.5	77	5.0	0.5	100	4	84
196	0.5	76	5.0	0.5	100	4	88

\* Ultimate neutralizing capacity expressed as weight in grams of polylactic acid capable of reacting with 40 g. sodium hydroxide (calculated from total amount of standard sodium hydroxide solution required to neutralize and saponify a known quantity of sample). Completely polymerized lactic acid and monomeric lactic acid have equivalent weights of 72 and 90, respectively.

TABLE II. PREPARATION OF METHYL LACTATE BY PASSING METHANOL VAPOR THROUGH POLYLACTIC ACID (CYLINDRICAL VESSEL WITH FRITTED-GLASS PLATE)

Expt. No.	Poly-lactic Acid as Lactic Acid Equivalent, Mole	Temp., ° C.	Methanol Introduced, Moles	Rate of Adding Methanol, Millimoles per Min.	Conversion to Methyl Lactate, %
1 <sup>a</sup>	0.5	140-150	7.5	15-18	77
2 <sup>a</sup>	0.47	140-150	5.0	11.1	72
3 <sup>a</sup>	0.5	135-148	5.0	16.0	70
4 <sup>a</sup>	0.5	140-150	6.0	26.0	70
5 <sup>a</sup>	0.5	120-126	5.0	20.0	73
6 <sup>a</sup>	0.5	110-112	6.25	11.0	89
7 <sup>a</sup>	0.5	110-112	6.85	23.6	90
8 <sup>a</sup>	0.5	98-102	8.75	20.0	87
9 <sup>a</sup>	1.0	110-120	12.5	30.5	86
10 <sup>b</sup>	1.0	110-118	13.3	56.0	82
11 <sup>c</sup>	1.0	110-118	39.0	43.0	79
12 <sup>d</sup>	0.5	125-130	13.2	67.0	81

<sup>a</sup> Toluenesulfonic acid (1 g. per mole of lactic acid) was used as catalyst.

<sup>b</sup> Sulfuric acid (1 ml. per mole of lactic acid) was used.

<sup>c</sup> Phosphoric acid (2 ml. of 85%) was used.

<sup>d</sup> Anhydrous zinc chloride (4 g.) was used.

in methanol (usually 70 grams polymer in 30 ml. of methanol), were fed continuously into the top of the tower. If not already present, the catalyst was dissolved in the polylactic acid prior to introduction into the tower. Methanol vapor was passed continuously (from a flask containing boiling methanol) into the tower near the bottom, and vapors of methanol and methyl lactate were withdrawn continuously from the top and passed into a continuous still. The methanol vapor from the top of the continuous still was recycled—that is, passed into the flask of boiling methanol and then as vapor into the bottom of the esterification or alcoholysis tower. The methyl lactate withdrawn from the bottom of the continuous still contained approximately 30% methanol and small quantities of water. Probably methyl lactate containing only traces of methanol would have been obtained with a more efficient column. The methyl lactate-methanol mixtures were redistilled, and the data thus obtained were used to calculate the yields given in Table III.

In some instances (experiments 221 and 222, Table III) the amount of methyl lactate recovered by distillation was small, and appreciable yields of distillation residue were obtained. It is believed that acidic material, such as sulfur dioxide, was carried over with the methanol and methyl lactate vapors and that this catalyzed the conversion of methyl lactate into compounds which were left as a residue in distillation. It was found advantageous to add basic material, such as sodium acetate, prior to distillation, especially when sulfuric acid had been used as catalyst. The advantages of neutralizing acid constituents and distilling under reduced pressures were discussed in a previous paper (25).

#### ETHYL LACTATE

The reaction of polylactic acid with the higher alcohols was not studied extensively, but ethyl lactate was prepared by the interaction of polylactic acid and ethanol. In the first preparation, 77 grams of polylactic acid (equivalent to 1 mole of lactic acid), 115 grams of ethanol (2.5 moles), and 1 ml. of concentrated sulfuric acid were heated at 100° C. for 4 hours in a closed bottle. The mixture was treated with 4 grams of anhydrous sodium acetate and distilled. The conversion into ethyl lactate distilling at 65° (28 mm.) was 57%; the distillation residue amounted to 39 grams.

In the second preparation, an ethanol solution containing 73.5 grams of polylactic acid (equivalent to 1 mole of lactic acid) and 0.5 ml. of concentrated sulfuric acid was passed into the top of the packed tower while ethanol vapor was passed into the bottom.

The temperature was 120° to 126° C., and the operation lasted 2.9 hours. The conversion into ethyl lactate was 77%. On the basis of starting material not recovered as distillation residue, the yield was 86.5% of theoretical.

#### CRUDE LACTIC ACID AS STARTING MATERIAL

As Tables II and III show, lactic acid of moderate purity can be converted into methyl lactate continuously and in high yields by dehydration and polymerization followed by methanolysis. Because of its lower cost (18), crude lactic acid is preferable to edible or other refined grades as a raw material. Several samples of crude lactic acid were less suitable experimentally, however, because their dehydration rates were lower, and solids separated during the dehydration and subsequent treatment with methanol. Results obtained with polylactic acid prepared from several samples of crude lactic acid by the batch distillation of water (usually after the addition of concentrated sulfuric acid) under a pressure of 10 to 20 mm. of mercury are given in Table IV. The methanolyses were carried out by passing methanol solutions of the polylactic acid through the reaction tower used for the experiments described in Table III. Although solids had been filtered from the methanol solutions, some precipitation occurred in the tower, requiring occasional cleaning by washing with water.

It was found advantageous to use more sulfuric acid than was required for catalysis with some of the samples of crude lactic acid. Presumably the larger quantities of sulfuric acid were required because of the sodium chloride, organic nitrogen compounds, or other materials capable of reacting with sulfuric acid. Considerable quantities of hydrogen chloride were volatilized with the methyl lactate when sodium chloride was present in the crude lactic acid. Hydrogen chloride in the distillate facilitated the hydrolysis of methyl lactate and made analysis for chloride necessary when the lactic acid content of the distillate was determined by titration and saponification.

TABLE III. METHYL LACTATE FROM POLYLACTIC ACID AND METHANOL VAPOR (PACKED TOWER EXPERIMENTS)

Expt. No.	Poly-lactic Acid as Lactic Acid Equivalent, Moles	Catalyst (H <sub>2</sub> SO <sub>4</sub> ), Ml.	Temp., ° C.	Addition of Poly-lactic Acid		Conversion to Methyl Lactate, %
				Total time, hr.	Millimoles per min.	
221	1.0	1	110-125	1.5	11.0	53
222	1.0	1	110-125	2.5	6.7	55
228	1.0	1	110-125	1.0	16.7	85
230	2.0	2	110-125	2.0	16.7	83
232	4.0	4	110-125	2.6	18.0	82
238	1.0	1	100-105	2.0	8.3	92
239	2.0	2	125	3-3.5	9.5-11	88
240	2.0	2	98-105	4-4.25	7.8-8.3	89

<sup>a</sup> Toluene sulfonic acid, 1 gram.

TABLE IV. ALCOHOLYSIS OF POLYLACTIC ACID PREPARED FROM CRUDE LACTIC ACID

Expt. No.	Poly-lactic Acid		Coned. H <sub>2</sub> SO <sub>4</sub> , Ml.	Temp., ° C. <sup>a</sup>	Time, Hr.	Lactic Acid Volatilized <sup>b</sup> , %	Methyl Lactate Yield, %	
	Lactic acid equiv- alent, moles	Concn. as lactic acid, %					A <sup>c</sup>	B <sup>d</sup>
1 <sup>e</sup>	2	116	2	98-106	12	..	67	73
2 <sup>e</sup>	5	115	5.1	100-112	10.5	..	57	74
3 <sup>f</sup>	1	91	1	101-109	4	73	29	55
4 <sup>f</sup>	2	89	8	88-105	3.2	92	64 <sup>g</sup>	74 <sup>g</sup>
5 <sup>f</sup>	1	84	14	87-109	2.5	85	79 <sup>h</sup>	80 <sup>h</sup>
6 <sup>f</sup>	2	117	2	98-103	5.5	..	78	85

<sup>a</sup> Temperature at a point midway between the bottom and top of the reaction tower.

<sup>b</sup> Determined by titration and saponification of the distillate.

<sup>c</sup> Based on polylactic acid passed into the tower.

<sup>d</sup> Based on polylactic acid not recovered as distillation residue (90 g. residue taken 1 mole).

<sup>e</sup> Crude material contained 26% lactic acid prior to concentration (supplied by Sheffield Farms, Inc.).

<sup>f</sup> Crude material contained 23% lactic acid prior to concentration (supplied by the Clinton Company).

<sup>g</sup> Distillation residue recycled once.

<sup>h</sup> Distillation residue recycled twice.

<sup>i</sup> Crude material contained 81.3% lactic acid prior to concentration (supplied by the Clinton Company).

Although the use of crude lactic acid is more troublesome, it gives moderately high yields of methyl lactate (Table IV) under suitable conditions. The present work indicates that addition of sulfuric acid in quantities greater than used for catalysis is helpful, that filtration of solids from the methanol solution of the polylactic acid may be required, that treatment with sodium acetate or similar agent prior to distillation is beneficial, that entraining agents such as benzene may be used advantageously to distill water from methyl lactate, and that distillation of methyl lactate under reduced pressure is preferable.

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